Unified charge transport in disordered organic field-effect transistors and light-emitting diodes

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Chapter 1

Introduction

Summary

Since the 1990's, after field-effects and electroluminescence were discovered in conjugated polymers, substantial effort has been devoted to the use of these materials in electronic devices. In this chapter we present a brief overview regarding the field of conjugated polymers and describe the operation principles of two (opto)electronic devices comprising semiconducting polymer films as the active component, namely light-emitting diodes and field-effect transistors. Finally, a short outline of the thesis is given.

1.1 Organic semiconductors

Electrical conduction in organic materials has been reported for the first time in the 1950's and early 1960's, when photoconductivity and electroluminescence were detected in organic crystals, such as naphthalene and anthracene [1–4]. Although the crystals showed high charge carrier mobility, their processability was very poor with little potential for applications. In the mid-1960's molecularly doped polymers formed by small organic pigments dispersed in an insulating polymer matrix were developed for xerographic applications [5]. They possessed the semiconducting properties of small organic molecules and the mechanical properties of polymers. A breakthrough in the field of conducting polymers was made in 1977, when the first highly conductive polymer, chemically doped polyacetylene, was reported [6]. In the 1980's electroluminescence was reported from double layer vacuum-sublimed molecular thin film devices [7], and from conjugated polymers such as poly(*p*-phenylene vinylene) (PPV) [8]. Since then, a new perspective has been opened on the applicability of organic molecules and semiconducting polymers into (opto)electronic devices.

Beside the research in the field of polymer light-emitting diodes (LEDs), several other research fields based on polymer semiconductors have been developed in the past decade, such as field-effect transistors (FETs) [9–11] and photovoltaics [12–14]. The polymers used in these applications are processed from solution, using spin coating, film casting or inkjet printing techniques, being able to provide large-area, flexible, lightweight displays and integrated circuits. Their low cost production, resulting mainly from the ease of processing, make them interesting for the electronic industry. But in order to be competitive, organic displays must provide comparable device performance with the already existing inorganic ones. These organic displays combine the mechanical properties of solution-processable organic materials with the electrical properties of semiconductors. Nowadays, the synthesis of new solution-processable polymers has shown that different color emission, high mobility and increased efficiency can be achieved in (opto)electronic devices. Some commercial application based on semiconducting polymers have already become available, such as a Philips shaver (2002) and a Philips mobile phone (2004), both featuring a polymer LED display.

In this thesis we focus on the charge transport through undoped (unintentionally doped) conjugated polymers that are used as active materials in LEDs and FETs. Conjugated polymers are organic macromolecules which have a framework of alternating single and double carbon-carbon bonds. Single bonds are referred to as σ-bonds and are associated with a highly localized electron density in the plane of the molecule, and double bonds contain a σ-bond and a π-bond, where the π-bond is the overlap between p_z orbitals of neighboring atoms along the conjugation path. The conjugation of single and double bonds establishes a delocalization of the electrons situated above and below the plane of the molecule. π-bands are either empty (called the Lowest Unoccupied Molecular Orbital - LUMO) or filled with electrons (called the Highest Occupied Molecular Orbital - HOMO). The band gap of these materials determined from optical measurements is within the semiconductor range of 1–4 eV, which covers the whole range from infrared to ultraviolet region. A well-known ex-

ample of a conjugated polymer is polyacetylene, which consists only of a single chain of alternating single- and double-bonds (Figure 1.1). The polyacetylene has a degenerated ground state. But most of the molecules studied throughout this thesis do not have this ground state. In Figure 1.2 some examples of the most commonly used conjugated polymers are presented.

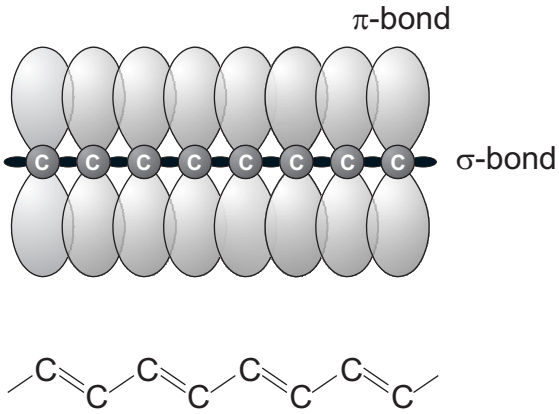

Figure 1.1: Schematic representation of the electronic bonds between carbon atoms (above) in polyacetylene (below).

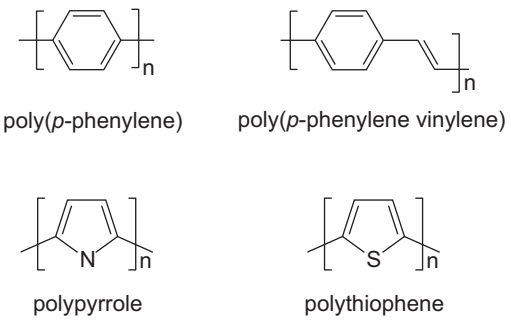

Figure 1.2: Chemical structure of some commonly used conjugated polymers. Hydrogen atoms are not shown and can be replaced by different sidegroups.

1.2 Polymer light-emitting diodes

Since the discovery of electroluminescence in poly(*p*-phenylene vinylene) (PPV) in 1990 [8] extensive research has been carried out to understand and develop polymer light-emitting diodes (LEDs). A typical single-layer polymer LED is presented in Figure 1.3a. A thin polymer film is spin-coated from solution on a semitransparent bottom electrode, normally indium-tin-oxide (ITO), which forms the anode. A low

work-function metal (calcium or barium) is evaporated on top of the polymer and serves as cathode.

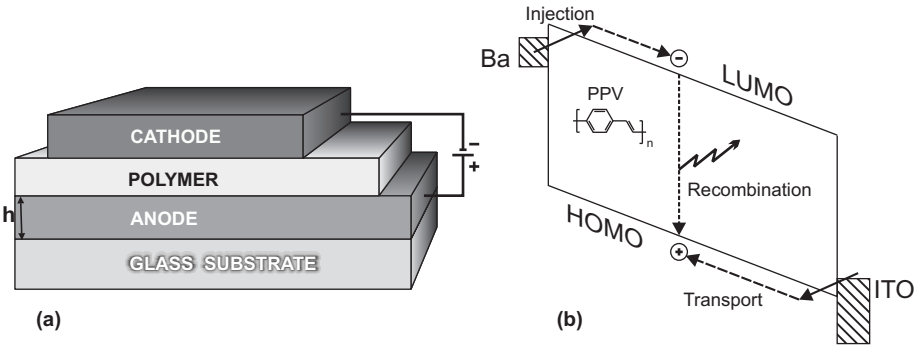

Figure 1.3: Schematic representation of a polymer LED (a) and energy-band diagram of a PPV-based LED (b).

The main processes that govern the operation of the polymer LED are: charge injection, charge transport and recombination (Figure 1.3b) [15]. Under forward bias, holes and electrons are injected from the anode and cathode, respectively. The charge carriers move through the polymer film and recombine. The energy released upon recombination is emitted as a photon through the semitransparent electrode. The emitted light can be tuned from red to blue, depending on the band gap of the polymer. In order to be injected from the electrodes, the charges must surmount or tunnel through a barrier at the polymer/electrode interface, which is determined by the position of the highest occupied molecular orbital (HOMO or π orbital) and the lowest unoccupied molecular orbital (LUMO or π^* orbital) and the position of the electrode metal work-functions. In the case of PPV, which has the HOMO level at 5.2 eV and the LUMO level at 2.9 eV, a good choice for the hole injecting electrode is ITO due to its work-function of ≈ 5 eV, resulting in a small injection barrier for holes [16]. In order to have a small interface energy barrier for electrons, low work-function metals such as calcium (Ca) or barium (Ba) ($\phi_M \approx 3$ eV) must be used in the case of PPV. A schematic band diagram of a PPV-based LED under forward bias using ITO as a hole injector and Ba as an electron injector is shown in Figure 1.3b. In this case the injection does not limit the device performance. However, the control of the anode/polymer and polymer/cathode interfaces is important, since it controls the charge injection process. A consequence is that it may influence the electronic structure and luminescence properties of the polymers [17,18]. The chemistry involved at these interfaces is always related to the nature of the polymer and the metal in question, the cleanliness of the materials and the evaporation process [19]. Despite these chemical interactions between the polymer and the metal, measurements of the built-in electrical field showed that the electrode-polymer interfaces still scale with the work-functions of the electrodes [20].

Besides injection, the charge transport in disordered organic semiconductors has been studied extensively. From current-voltage measurements, it has been demon-

strated that the current flow in the LED is limited by the bulk transport and not by injection for contacts barriers smaller than 0.4 eV [21–23]. Due to relatively low mobility in these disordered semiconductors, the charges build up in the device and space-charge effects occur in polymer LEDs. To achieve high efficiency, a balanced electron and hole transport is required. In that case, the recombination of the charges takes place close to the middle of the semiconductor. But when the charge transport is not balanced, the recombination moves toward one of the electrodes, where the luminescence is quenched by the electrode. The origin of this effect is dipole quenching and leads to a reduced efficiency [24].

One way to overcome this problem is to introduce a number of active layers, each optimized for its own functionality [7,25]. For example, in the case of a trilayer diode, the highly emissive layer is sandwiched between a hole- and electron-transporting layers. The hole transporting layer adjacent to the anode must have high mobility for holes, whereas the electron transporting layer adjacent to the cathode must have high mobility for electrons. In this way, the holes and electrons meet each other in the highly emissive layer and the recombination zone can be shifted away from the cathode, where excitons are quenched. As a result, high efficiencies and low operating voltages can be simultaneously achieved. This approach has been successfully applied in small molecule devices [26] and polymer-based devices [27]. Recently, a record efficiency of 110 lm/W was reported for doped small molecules LEDs, which is over 50% higher than for inorganic LEDs [28].

1.3 Polymer field-effect transistors

The concept of the field-effect transistors (FET), first proposed by Lilienfield in 1930 [29] and later studied by Shockley and Pearson in 1948 [30], started to be used as a practical application only in 1960 [31]. The most popular FET is the metal-oxide-semiconductor FET (MOSFET), also known as the metal-insulator-semiconductor FET (MISFET), in which the gate electrode is electrically insulated from the conducting channel by an insulating oxide layer (Figure 1.4). The basic idea of a field-effect transistor is to modulate the current that flows between two ohmic contacts, the source and the drain electrodes, by applying a voltage to a third contact, the gate electrode. In this way charge carriers can be accumulated or depleted in the semiconductor close to the semiconductor/insulator interface. In fact, this device can be considered as a capacitor, where one plate is the conductive channel in the semiconducting layer and the other is the gate electrode.

The operation of an unintentionally doped p-type MISFET can be explained by analyzing the energy band diagram which is schematically presented in Figure 1.5 [32]. In equilibrium the Fermi levels of the gate metal and the semiconductor align due to the charge carriers, which move to or from the semiconductor/insulator interface. When a voltage, called flat-band voltage, V_{fb}, equal to the difference between the Fermi levels of the materials is applied no band bending will be present in the semiconductor at the semiconductor/insulator interface (Figure 1.5a). The charges that are present in the device under biasing conditions are those in the semiconductor and

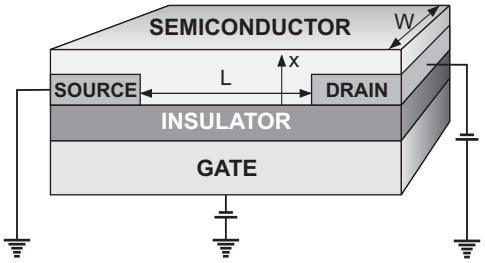

Figure 1.4: Schematic representation of a polymer FET

those with equal opposite sign on the gate. By applying positive or negative gate voltages, induced charge carriers electrostatically accumulate or deplete in the semiconductor close to the semiconductor/insulator interface giving rise to band bending in the semiconductor. If a negative bias is applied to the gate, the voltage drop across the insulator will accumulate holes at the semiconductor/insulator interface and the energy bands are bent upwards (Figure 1.5b). The additional positive charges accumulated in this region are supplied by the drain- and source-ohmic contacts. These charges are mobile and under a small drain bias will give rise to the field-effect current. If a positive voltage is now applied to the gate, the positive charges are depleted from the semiconductor/insulator interface and the energy bands bend downwards. In this case the transistor is biased in the depletion mode (Figure 1.5c). In this way the field-effect current is varied in the source-drain channel.

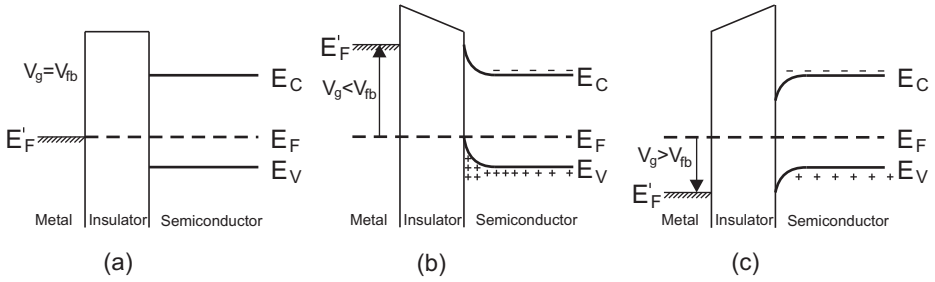

Figure 1.5: Energy-band diagram of a p-type MIS FET working in: a) flat-band ($V_g = V_{fb}$); b) accumulation ($V_g < V_{fb}$); c) depletion ($V_g > V_{fb}$).

1.4 Scope and outline of this thesis

Charge transport in conjugated polymers is regarded as a hopping process between localized states, which are thought to consist of individual conjugated segments. Due to different orientations of the conjugated segments with respect to each other and to

their different lengths, a distribution of localized energy states will be present in the polymer. In this way the charge carrier transport through the semiconductor bulk material is related to the order in the system. Considering the amount of disorder, three classes of organic semiconducting polymers are distinguished: amorphous, crystalline and partially-ordered (or partially crystalline). The scope of this thesis is to study the charge transport in amorphous conjugated polymers in various device configurations. Different transport parameters, such as charge carrier density and charge carrier mobility are analyzed in: field-effect transistors, single and double layer light-emitting diodes, in-plane diodes and ambipolar transistors. In order to relate the transport characteristics to the morphological and energetic disorder present in the polymer films, a number of different polymers are analyzed.

In *Chapter 2*, the relevant charge transport models for disordered organic semiconductors are presented. Then, we present two theoretical models frequently used to analyze the charge transport in polymer based LEDs and FETs: hopping in a Gaussian DOS is applied to explain the field and temperature dependence of the carrier mobility in LEDs, while the hopping in an exponential DOS explains the gate voltage and temperature dependence in FETs. Because the polymers characterized in these devices belong to the same class of disordered π conjugated systems, one unified description should be used to describe their electrical transport characteristics. But this will be discussed in *Chapter 4*.

Chapter 3 describes the polymers used in this thesis, the device preparation and the procedures used to measure the devices.

A fundamental process in the charge transport in disordered polymer FETs and LEDs, the dependence of the charge mobility on the charge density, is addressed in *Chapter 4*. In order to determine the local mobility in FETs, the charge carrier density distribution perpendicular to the semiconductor/insulator interface is calculated. It is shown that a major part of the charge carriers is located close to the interface and they have the highest mobility. In a space charge-limited (SCL) diode based on disordered polymers the enhancement of the hole current at high bias was attributed in the earlier reports to the field dependence of the mobility. We demonstrate that the charge carrier density dependence of the mobility is dominant at room temperature, while at low temperatures the field dependence of the mobility must be considered. Then one polymer is used as active material in a LED and a FET in order to understand why fundamentally different properties such as charge transport and mobility values are reported for these devices. We demonstrate that the strong increase of the mobility with increasing charge density is responsible for the observed large mobility differences obtained from the LEDs and FETs. The exponential density of states, which consistently describes the field-effect transport measurements, is shown to be a good approximation of the tail states of the Gaussian density of states used to describe the LED transport measurements.

To relate the transport characteristics to the morphological and energetic disorder present in the polymer film, in *Chapter 5* the charge transport for different disordered polymers is studied. Optimization of chemical structure, annealing, and solvent lead

to high mobility of 9×10^{-10} m^2/Vs in a hole-only diode and 1×10^{-6} m^2/Vs in a FET. Comparison of the electrical measurements in planar metal-polymer-metal devices with those of field-effect transistors demonstrates that the enhanced current measured in planar devices originates from a high surface charge carrier density at the polymer/substrate interface. The presence of such a conducting channel due to charging of the surface obscures the intrinsic in-plane conducting properties of PPV.

In *Chapter 6* the electrical properties of a dual-layer PPV LED are discussed. We combine two PPV layers, one with high mobility and the other with high luminescence. As a result, high light output efficiencies and low operating voltages are simultaneously achieved with relatively thick active layers. Another advantage of this dual-layer LED is that both polymers emit light. This means that a short-circuit in the luminescent layer does not lead to a catastrophic failure of the diode.

PCBM is a soluble C_{60} derivative which is used as electron acceptor in bulk heterojunction solar-cells. Recently, PCBM started to be used as active organic material in FETs. In *Chapter 7* it is demonstrated that a methanofullerene based FET exhibits ambipolar transport characteristics. The devices operate in hole or electron accumulation, depending on the biasing conditions. The characteristics of PCBM ambipolar FETs are also analyzed in CMOS-like inverters.

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